Ammonia formation over supported platinum and palladium catalysts

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ABSTRACT

We report experimental results for the formation of ammonia from nitric oxide and hydrogen, and from nitric oxide, water and carbon monoxide over silica, alumina and titania supported platinum and palladium catalysts. Temperature programmed reaction experiments in gas flow reactor show a considerable formation of ammonia in the temperature range 200–450 °C, which is suppressed by the presence of excess oxygen. However, oxygen sweep experiments show that for the titania supported catalysts minor amounts of oxygen promotes the ammonia formation at low temperatures. In situ DRIFT spectroscopy measurements indicate that cyanate species on the support play an important role in the ammonia formation mechanism. This work shows that alumina supported palladium is a promising system for passive selective catalytic reduction applications, exhibiting low-temperature activity during the water–gas-shift assisted ammonia formation reaction. Conversely, titania supported samples are less active for ammonia formation as a result of the poor thermal stability of the titania support.

1. Introduction

Combustion of petrol and diesel in vehicles results in the formation of harmful products, including nitrogen oxides (NO_x), which are known to be responsible for various environmental issues such as photochemical smog and acid rain [1,2]. At present, the fuel economy of passenger cars can be improved by ensuring that the combustion takes place in the presence of excess oxygen, so-called lean operation [3]. Practically, lean operation makes it challenging to reduce NO_x to N_2 over the conventional three-way catalyst [4]. Thus it is necessary for new strategies to be developed whereby the fuel economy can be improved whilst the tailpipe emissions are kept sufficiently low [5,6]. Selective catalytic reduction of NO_x with ammonia (NH_3-SCR) is currently the preferred technology for NO_x abatement from stationary sources and larger vehicles including trucks and buses [7]. Ammonia-SCR relies on the ability of the catalyst to selectively reduce NO_x with NH_3 to form N_2 in the presence of elevated levels of O_2 [8,2]. However, due to concerns with the safety and toxicity associated with ammonia transportation and storage, the NH_3 is stored in the form of urea-in-water solution on-board the vehicle. Urea solution is injected into the exhaust gas where it thermally decomposes and hydrolyses to form the

ammonia required for NH_3-SCR [9,10]. Although this solution has been accepted for heavy-duty vehicles, difficulties arise when applied to smaller passenger vehicles. Some of the problems encountered are due to extra weight associated with the need for an additional urea storage tank and injection system, which is complex, costly and may affect driving performance negatively, and the risk of creating an NH_3 slip [2,4,11]. Ammonia emissions are undesirable since NH_3 is a toxic air pollutant and is known to contribute to the production of secondary particulate matter [12,13].

Passive SCR is a newly developing technology that may contribute to solving some of the aforementioned problems [14]. The concept of this technique is to generate NH_3 on-board the vehicle by utilizing the NO_x that is readily available in the exhaust stream whilst the engine undergoes rich operation (low air-to-fuel ratio). The formed NH_3 can then be stored on an SCR catalyst downstream and used to reduce slipped NO_x when the engine is set back to operate under lean conditions. If sufficient amounts of NH_3 can be produced during the rich periods and stored for complete reaction with NO_x to form N_2 during the subsequent lean periods, an external urea injection system may not be needed. It is well known that NH_3 can be formed over precious metal catalysts by the reaction between NO_x and H_2 provided that the stoichiometric requirement, i.e. $H_2/NO \geq 2.5$, is fulfilled. The overall reaction follows;

$$NO + \frac{5}{2} H_2 \rightarrow NH_3 + H_2O \qquad (1)$$

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If the criterion on the H_2/NO ratio is not fulfilled, selectivity to other nitrogen-containing products has been observed [11,15,16], for example N_2O and N_2 by the two reactions:

$$NO + \frac{1}{2}H_2 \rightarrow \frac{1}{2}N_2O + \frac{1}{2}H_2O \tag{2}$$

$$NO + H_2 \rightarrow \frac{1}{2}N_2 + H_2O \tag{3}$$

In automotive applications deviations in driving patterns result in conditions where the concentration of H_2 present in the exhaust feed does not meet the requirement for ammonia formation for significant periods. Despite this, passive SCR may play an important role in NO_x abatement provided that a direct supply of H_2 is not necessary. Carbon monoxide and water are also present in the exhausts during rich operation [17] and H_2 can be formed by the water-gas-shift (WGS) reaction;

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4}$$

Hence, water could be a viable hydrogen source for the further formation of NH_3.

Previously Okumura et al. showed that SiO_2 and Al_2O_3 supported Pt and Pd catalysts have high selectivity to form NH_3 when in the presence of NO and H_2 at temperatures between 400 and 500 °C as compared to the corresponding Ir and Rh catalysts. In addition, Macleod et al. [2] showed that there is a synergy between Al_2O_3 and TiO_2 supports, which leads to further elevated formation of NH_3 in the presence of NO, CO and H_2O. This benefit can be ascribed to the hydrolysis of isocyanate groups, which is an additional well-documented route for NH_3 formation [15,18,17]. Although this process requires a catalytically active site (S) to form the initial surface isocyanate species (Eqs. (5) and (7)), the reaction steps responsible for the formation of NH_3 can take place both in the gas phase (Eq. (6)) and *via* an adsorbed species on the catalyst surface (Eq. (8));

$$S\text{-NCO} + H_2O \rightarrow S\text{-OH} + HNCO \tag{5}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{6}$$

$$S\text{-NCO} + H_2O \rightarrow S\text{-NH}_2 + CO_2 \tag{7}$$

$$S\text{-NH}_2 + H_2O \rightarrow S\text{-OH} + NH_3 \tag{8}$$

The objective of the present study is to investigate whether or not NH_3 can be formed over a wide temperature window from $NO + H_2$ and $NO + H_2O + CO$ gas mixtures over supported Pt and Pd catalysts, specifically addressing the role of the support material. This is carried out by a systematic comparison of silica, alumina and titania as support materials. Also, the influence of the presence of O_2 on the ammonia formation is studied.

2. Experimental

2.1. Catalyst preparation and characterisation

Supported Pt and Pd powder catalysts were prepared by incipient wetness impregnation of each of the following support materials: Al_2O_3 (Puralox SBa200), SiO_2 (Kromasil) and TiO_2 (Hombifine). The supports were thermally treated in air at 600 °C to remove impurities and stabilise the structure prior to impregnation. Thereafter, the saturation point of each support was determined and they were then suspended in the corresponding volume of aqueous solutions of either $(NH_3)_4Pt(NO_3)_2$ or $(NH_3)_4Pd(NO_3)_2$ to ensure all solution would be taken up by the support. All prepared catalysts were frozen in liquid N_2 and subsequently freeze-dried for approximately 12 h to ensure complete sublimation of water. The powder samples were then calcined at 550 °C in air for 1 h.

The powder catalysts were then coated onto cordierite monolith substrates. This was done by preparing solutions consisting of the powder catalyst, suitable binder materials based on support composition (Al_2O_3; Disperal P2, SiO_2; Colloidal SiO_2 and TiO_2; TiO_2 sol), water and ethanol. The monolith was then carefully immersed into the slurry, allowing the catalyst-containing liquid to be dispersed evenly throughout the channels by capillary forces. The monolith was then dried in air at 90 °C for two minutes to remove the water and ethanol, before being briefly calcined in air for a further two minutes at 500 °C and weighed. If necessary, the process was repeated until the desired mass of catalyst and binder was deposited (200 ± 3 mg). Once coated, the monoliths were calcined in air at 600 °C for 2 h to ensure complete removal of water. The specific surface area of the prepared samples was measured by nitrogen physisorption at −196 °C using an ASAP 2010 (Micrometrics) sorptometer. Prior to adsorption, all samples were dried at 200 °C for 2 h under vacuum in order to remove any residual water. Respective surface areas were then determined according to the standard Brunauer–Emmett–Teller (BET) method [19] using $P/P_0 = 0.05$–0.20. The specific surface area of the pure support materials; both fresh and after calcination in air at 600 °C for 1 h was measured to determine the thermal stability of the supports. The prepared powder catalysts were characterised directly after calcination.

Transmission electron microscopy (TEM) analysis was carried out to determine the average noble metal particle size for each catalyst. A small amount of sample was dispersed in ethanol in an ultrasonic bath for 20 seconds. One drop of the suspension was then placed onto a Cu-grid coated with lacey carbon. Between 6 and 14 images of each sample were recorded at different magnifications: 36×36–294×294 nm. Additionally, energy dispersive spectroscopy (EDS) analyses were acquired at each position investigated to locate and confirm the presence and type of metal particles.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was used to confirm the noble metal content of all samples. A mass of 0.1–0.15 g of finely ground sample was digested in a solution containing HNO_3 and HCl at 200 °C for 20 min in a Milestone Ethos Plus microwave digestion unit. The resultant clear sample solution was then diluted using pure water (18.2 MΩ) and the metal content was quantified with an Agilent 720 ES ICP-OES instrument. Emission signals from the sample were compared to the signal from certified calibration standards containing 0–10 mg/l Pd or Pt.

To compliment the afore-mentioned characterisation techniques, powder X-ray diffraction (XRD) was also performed using a Bruker XRD D8 Advance instrument with monochromatic CuKα_1 radiation. The 2θ range of interest was 15°–85° and the step size and time employed were 0.041 and 1 s, respectively. The rotation speed of the sample during measurement was 60 rpm.

2.2. Kinetic measurements in gas flow reactor

Continuous gas flow reactor studies were carried out to determine the activity of the prepared catalysts. The reactor setup employed in this investigation has previously been described by Kannisto et al. [20]. The system consists of a quartz tube surrounded with a heating coil and insulation. It contains two thermocouples to measure the temperature 10 mm before and in the centre of the monolith sample. Two uncoated (blank) cordierite monoliths were placed on either side of the sample monolith in the quartz tube in order to reduce otherwise significant heat losses and achieve a nearly isothermal sample. The inlet gas composition was controlled using mass flow controllers (Bronkhorst Hi-Tech LOW-ΔP-FLOW) and the outlet gas composition was analysed using an FTIR gas-analyzer (MKS 2030 HS). All experiments were carried out